Review

Carbon materials in composite bipolar plates for polymer electrolyte membrane fuel cells: A review of the main challenges to improve electrical performance

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ABSTRACT

The technology of polymer electrolyte membrane (PEM) fuel cells is dependent on the performance of bipolar plates. There is a strong relationship between the material used in the manufacturing of the bipolar plate and its final properties. Graphite–polymer composite bipolar plates are well-established commercial products. Several other carbon based fillers are tested. Carbon nanotubes, carbon fibers, carbon black, graphite nanoplatelets and expanded graphite are examples of such materials. Structural characteristics of these particles such as morphology and size have decisive influence on the final properties of bipolar plates. Furthermore, the volumetric fraction of the filler is of prime importance. There is plenty of information on individual aspects of specific composite bipolar plates in the literature. Notwithstanding, the analysis of structure–property relationship of these materials in a comprehensive source is not found. In this paper, relevant topics on the structural aspects of carbon based fillers and how they influence the final electrical performance of composite bipolar plates are discussed. It is intended that this document contribute to the development of new and maximized products to the PEM fuel cell industry.

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Contents

1. Introduction

Bipolar plates are key components of PEM fuel cells. They are responsible for functions of vital importance to the long-term operation of these electrochemical devices. They play major roles in water and gas management, mechanical stability and electrical

performance of fuel cells [1–3]. A very assorted pack of material's properties must be considered for the successful design of these components, namely, electrical and thermal conductivities, gas impermeability, mechanical strength, corrosion resistance and low density. The technical targets are defined by the United States of America Department of Energy (DOE) [4] as shown in Table 1.

The list of materials available for the design of bipolar plates is relatively long. Pure graphite was the first option thanks to a suitable combination of thermal and electrical properties. However, its inherent brittleness and high manufacturing costs of machining operations bring about prohibitive features for a massive large-

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Table 1
US DOE technical targets for composite bipolar plates.

Property	Value
Weight	<0.4 kg kW^{-1}
Flexural strength	>25 MPa
Flexibility	3–5% deflection at mid-span
Electrical conductivity	>100 S cm^{-1}
Thermal conductivity	>10 W (m K)$^{-1}$
Gas permeability	<2 × 10^{-6} cm^3 cm^{-2} s^{-1} at 80 °C and 3 atm
Corrosion resistance	<1 μA cm^{-2}

scale production [5,6]. Several metallic alloys are envisaged as possible bipolar plate materials combining excellent gas impermeability and mechanical resistance. Stainless steels [7–9], aluminum [10], nickel [11], copper [12], titanium [13], bulk amorphous alloys [14] and even carbon steels [15] are investigated in the literature for this application. Most of the scientific reports focus on stainless steels due to a suitable conjunction of technical performance and ease of manufacturing at a low cost [16]. It is not to be disregarded, though, that metallic bipolar plates undergo corrosive processes in the PEM fuel cell environment [17]. Hence, the growth of a less conductive oxide layer negatively affects the electrical conductivity of the component. Furthermore, ions that are leached from the metallic surface may poison the catalyst layer in the membrane electrode assembly [18]. Even very small quantities of metallic ions may greatly reduce the overall power density of the fuel cell [19]. As a result, surface modifications or protective coatings are necessary to ensure that these drawbacks do not shorten the service life of the bipolar plate [20].

Graphite–polymer composites with either thermoplastic or thermoset matrices are advantageous over metallic materials with regard to corrosion resistance and low weight. Additionally, they may be produced in an economical way, from compression, transfer or injection molding processes, depending on the number of units to be manufactured [21]. There are several different types of commercially available graphite–polymer composite bipolar plates such as polypropylene (PP), polyphenylene sulfide (PPS), polyvinylidene fluoride (PVDF) and phenolic resin [22–25]. Nevertheless, they are more permeable to gases, and present lower bulk electrical conductivity and mechanical resistance than metallic plates. However, the mechanical strength for stationary applications is perfectly adequate. It is only envisaged as a problem for if one considers the vibrations typical of vehicle applications when the fuel cells replace internal combustion engines [26]. So, the uppermost handicap is the lack of electrical conductivity, which is critical independently of the final application of the device [27]. Despite the well-established commercial products available to the manufacturing of PEM fuel cells, there is a constant seeking for the development of better composites with maximized electrical conductivity. The pathway to tailor such advanced materials is to incorporate other carbon based conductive fillers, besides conventional graphite, in the polymer matrix. These are carbon black (CB), multi-walled and single-walled carbon nanotubes (MWCNT and SWCNT), carbon fibers, expanded graphite and combinations thereof [28–32]. The conductive network and mechanical strength of the composite depend on the content, morphology, processing and size of the added particles. This very complex behavior is often investigated in the literature for specific filler-matrix pairs. However, there is still much to learn in order to clarify the mechanisms that govern the electrical behavior of carbon-filled bipolar plates in a comprehensive way. This work discusses the relationship between particle nature, size, morphology, processing and the interaction with the polymer matrix in order to help the development of optimized composite bipolar plates for the PEM fuel cell industry.
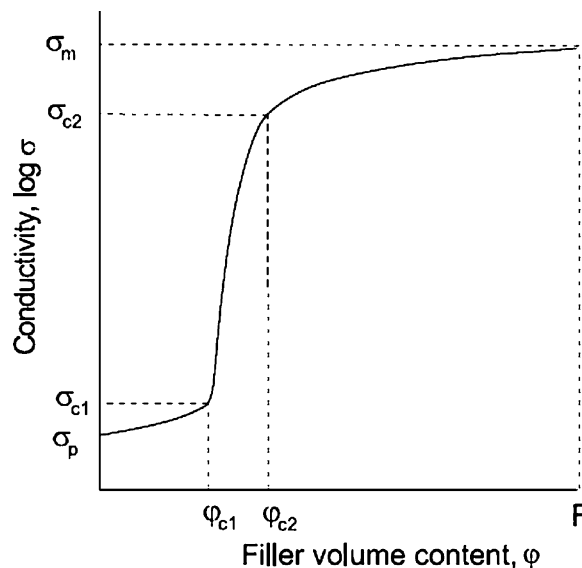

Fig. 1. Dependence of the conductivity of polymer matrices with the volume content of a conductive filler (Reproduced from Mamunya et al. by permission of Elsevier Science, UK [34].).

2. Percolation phenomena in conductive polymer composites (CPCs)

The conduction mechanism of CPCs is explained by the classical percolation theory [33]. It is assumed that the composite behaves as an insulator when the volume fraction of the conductive filler is below a specific value, known as the percolation threshold (φ_c). Above this critical content, an infinite conductive cluster is formed and the composite becomes conductive. This behavior is schematically shown in Fig. 1. The maximum electrical conductivity (σ_m) is achieved as the filler content (F) increases above the percolation threshold. Below this value the conductivity of the composite is mainly determined by the conductivity of the polymer matrix (σ_p). According to Efros and Shklovskii [35], the sharp conductivity increase occurs within the concentration range $\varphi_{c1} < \varphi_c < \varphi_{c2}$ called the smearing region. This region is indicated in Fig. 1.

Accurate identification of this value is the goal of many investigations on the electrical behavior of CPCs. Some general trends may be identified. Yet particular features regarding the nature of polymer matrices and conductive fillers should not be neglected. In this section different aspects of percolation phenomena of several polymer systems are reviewed. The information may not be directly obtained from references on composite bipolar plates. However, the findings outlined below are closely related to the electrical behavior of CPCs and, consequently, may be used to understand and improve the electrical performance of composite bipolar plates.

Lee et al. [28] conducted an investigation on the electrical performance and flexural strength of a compression molded epoxy resin–graphite composite bipolar plate reinforced with CB, MWCNTs and carbon fiber (CF). The electrical conductivity was shown to increase with the addition of carbon black up to a concentration of 5 vol.%. Above this content, a steep decrease was observed. Small carbon black particles help to make conducting tunnels between graphite particles, increasing conductivity. As the volume fraction of these particles increases, they are not wet by the epoxy resin in the same way, leading to an incomplete compaction that deteriorates the electrical performance of the composite. Similarly, the addition of MWCNTs causes an improvement of the electrical conductivity up to a concentration of 2 vol.%. If the filler loading increases, the electrical performance of the composite is reduced. Low contents of MWCNTs facilitate the dispersion in the polymer
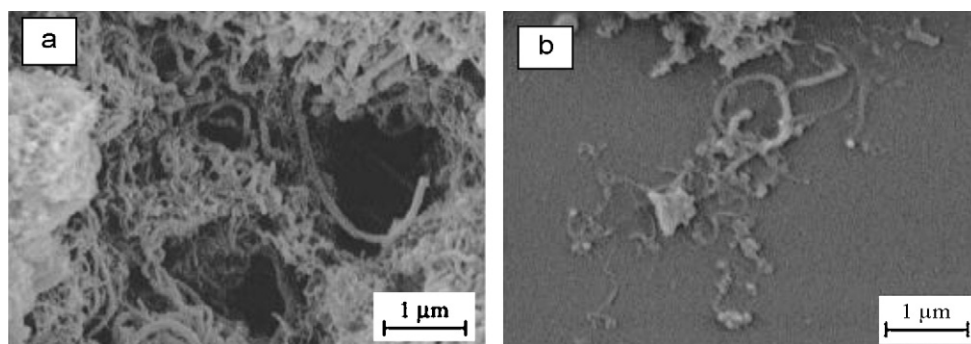
Fig. 2. SEM micrographs of (a) pristine MWCNTs and (b) reduced aspect ratio of MWCNTs after acid treatment (Reproduced from Zhu et al. by permission of Elsevier Science, UK [45].).

matrix, forming conducting channels between graphite particles. The aggregation of MWCNTs particles at higher filler loadings was responsible for the decrease of the electrical conductivity of the bipolar plate. A similar effect was observed after the addition of carbon fibers. In the same way, Allaoui et al. [36] reported a percolation threshold between 0.5 and 1 wt.% for an epoxy–MWCNT composite. The high aspect ratio of MWCNTs allows for reaching such a threshold even with smaller filler contents. Such behavior was confirmed by Celzard et al. [37] and Munson-McGee [38]. The percolation threshold for rod-like particles with aspect ratios of 100 or more was determined to be 0.24–1.35 vol.%. Even lower values are often reported [39,40]. Deviations from the results published by Celzard et al. [37] and Munson-McGee [38] were ascribed by Gojny et al. [41] to the absence of molecular level considerations in the model developed by those authors. On a nanometric scale cohesive interactions between conductive particles and toward the matrix are of great importance. In this way, Brownian motion of the fillers and their cohesive forces caused by van der Waals and dipole–dipole interactions should be considered to describe the percolation behavior of high aspect ratio particles in a feasible scientific model. Such contributions were neglected in the model proposed by Celzard et al. [37] and Munson-McGee [38]. Gojny et al. [41] also investigated how functionalization affects the percolation threshold of carbon nanotubes (CNTs). It is well established that the dispersibility of CNTs within polymer matrices may be enhanced by the modification of their surfaces through functionalization with different chemical groups [42–44]. They observed that the aspect ratio of NH_2-functionalized MWCNTs was lower than that of the pristine nanoparticles. As a result, the percolation threshold of the composite prepared with the functionalized material was higher than that of the untreated nanotubes. The incorporation of amino groups was achieved by ball milling the nanotubes with ammonia. During this operation nanotubes were disrupted, thus lowering their aspect ratio. Another possible explanation for this phenomena was that the introduction of functional groups into the conjugated π-electron system typical of the graphitic structure of CNTs was combined with the formation of sp^3-carbons. These carbons are considered as defects in a conjugated π-electron system, reducing the ability for achieving effective electron transport between the conductive particles. Moreover, as functionalization improves affinity between filler and resin, an insulating surface layer may be formed on the nanotubes. Then, mechanical properties are improved. On the other hand, the tunneling of electrons between adjacent particles would be depressed. The sum of these factors accounts for the higher percolation threshold of functionalized CNTs. Even though functionalization is frequently used to enhance dispersion of CNTs in polymer matrices, the results from Gojny et al. [41] evidence the need for evaluating the effect of specific surface groups on the percolation behavior of conductive polymer composites. The reduction of the aspect ratio of CNTs after functionalization

was also reported by Zhu et al. [45] for polyimide based composites. They performed an acid treatment of the CNTs in a solution comprised of sulfuric acid and nitric acid. The percolation threshold of the composite prepared with modified CNTs was 7.0 wt.%, which is much higher than frequently reported. The reduction of the aspect ratio after functionalization was observed through scanning electron microscopy (SEM) micrographs as shown in Fig. 2.

A good example of successful functionalization treatment of carbon nanotubes was reported by Lee et al. [46]. Functionalization was performed through acid treatment by immersing the nanotubes in a mixture of H_2SO_4 and HNO_3. Treated particles were then mixed with polypropylene in a twin screw extruder. The electrical conductivity experienced a marked increase for the composite prepared with the functionalized nanotubes in comparison with the one prepared with untreated fillers. Moreover, the percolation threshold was affected very little by the chemical treatment and was determined to be approximately 2 wt.% for both conditions. They have also reported the benefit of using a coupling agent to change the surface energy of the nanotubes and enhance their dispersion in the matrix. Specifically, they used maleic anhydride grafted polypropylene (MA-g-PP) and maleic anhydride grafted styrene–ethylene–butylene–styrene (MA-g-SEBS) as compatibilizers. The first one is intended to yield strong hydrogen bonding between the hydroxyl groups of the nanotubes and maleic anhydride groups. MA-g-SEBS is a block copolymer with styrene at both ends and ethylene/butylene intercalated between the styrene groups. It is expected that the two ends containing aromatic rings will be compatible with carbon nanotubes while the rubbery ethylene/butylene block will be compatible with polypropylene. The results confirmed that the incorporation of the coupling agents shifted the electrical conductivity of the composite to higher values.

Sandler et al. [39] suggested that the percolation threshold of MWCNTs in an epoxy matrix may be further reduced by using aligned particles instead of entangled nanotubes. The alignment was achieved during the manufacturing process of the nanotubes that consisted of an injection chemical vapor deposition process. Bauhofer and Kovacs [47] reviewed the percolation phenomena in polymer–CNTs composites. They assessed more than 140 experimental results and found contradicting information concerning the dependence of the percolation threshold on the aspect ratio of the conductive particles. Some authors reported that increasing CNT length yielded a reduction of the percolation threshold [48] while others found an opposite trend [40]. This discrepancy would be due to the type of percolation threshold that the others evaluated. According to Bauhofer and Kovacs [47], percolation may be classified as statistical or kinetic. In the first case, filler particles are randomly distributed, forming conducting paths. In the latter case, the particles are free to move, leading to the formation of a conducting network at much lower concentrations. The occurrence of such movement would be neglected in the literature, leading to mis-

conceptions in the analysis of percolation phenomena. Statistical percolation would explain the results obtained by Bai and Allaoui [48] while kinetic percolation would lead to the increase of the percolation threshold with a decrease of CNT length verified by Martin et al. [40].

Li and Kim [49] proposed a model based on the average interparticle distance (IPD) to predict the percolation threshold of polymer nanocomposites containing 3D randomly distributed disc-shaped nanoparticles. They tested the validity of this model by comparing theoretical results with experimental data taken from electrical conductivity measurements of epoxy resin reinforced with graphite nanoplatelets (GNPs) of different aspect ratios. The main output is the parabolic decrease of the percolation threshold with the increase of the aspect ratio of the conductive filler. The authors modeled a typical GNP as a thin and round platelet yielding a 3D schematic of the conducting networks in the composite as shown in Fig. 3. It was clear that the aspect ratio of the filler was the critical factor to determine the percolation threshold of the composite. This finding confirms the results obtained for carbon nanotubes and graphene reinforced polymer matrix composites [37,38,50].

Graphene-polymer conductive composites were successfully produced by several authors as recently reviewed by Kuila et al. [51]. Graphene is a two-dimensional carbon nanofiller with a one-atom-thick planar sheet of sp^2-bonded carbon atoms. These atoms form a highly dense structure in a honeycomb crystal lattice. The electrical conductivity of graphene-filled polymer composites is reported to be higher than that of carbon nanotubes [52,53]. This outstanding electrical performance is due to the high aspect ratio of graphene sheets that is also responsible for the low percolation thresholds of this filler in polymer matrix composites.

Carmona and Ravier [54] described the relevance of carbon black morphology to explain the percolation threshold of CB-filled polymers. Moreover, they stated that the interaction of the conductive particles with the macromolecular chains depends on the processing conditions and, consequently, on the dispersion of the fillers within the organic matrix. In an attempt to clarify this behavior, Balberg [55] proposed a mechanism for the percolative properties of CB-filled polymers. In previous works [56,57] Balberg found that the structure of the CB is determinant for the electrical percolation threshold of this filler in polymer matrix composites. Carbon blacks are characterized as low structure or high structure particles. According to the authors, the more the isolated particle is spherical, the less structured it is. The percolation threshold was found to decrease with the increasing degree of carbon black structure, i.e., for non-spherical particles. This effect was explained in the Balberg's model by considering the interaction between neighboring particles. Elongated particles of high-structure carbon blacks would have a more intense contact than do spherical particles with the same volume. Chen et al. [58] and Zhang et al. [59] found a similar tendency on graphite nanosheets-filled poly(methyl methacrylate) (PMMA) and polyethylene terephthalate (PET), respectively. High aspect ratio fillers such as fibers or sheets provided better electrical performance to the composite than spherical or elliptical particles. The formation of a conductive network between the fillers is favored in elongated particles, thus diminishing the percolation threshold. Zhang et al. [60] observed this behavior in phenolic resin–graphite sheets composites. In the same way, Thongruang et al. [61] found similar conclusions by comparing the electrical conductivity of graphite and carbon fiber filled high density polyethylene. The same approach was used by Tchmutin et al. [62] to explain the percolation behavior of polypropylene-graphite and polypropylene-SWCNT composites. Yao et al. [63] confirmed these findings through transmission electron microscopy (TEM) images of MWCNT–PVDF nanocomposites. This result is reproduced in Fig. 4. They showed that as the aspect ratio of MWCNTs increases, the conducting paths between the nanotubes increase, thus reduc-

ing the percolation threshold of the nanocomposites. Nanotubes become much more tightly packed as their aspect ratio grows as seen from Fig. 4a–c. The aspect ratios of the MWCNTs of Fig. 4a–c are 62, 116 and 437, respectively. This effect is schematically shown in Fig. 5.

Al-Saleh and Sundararaj [64] recently reviewed the properties and applications of vapor grown carbon nanofibers (VGCNF)/polymer composites. This kind of conductive filler is intended to replace carbon nanotubes in conductive polymer composites due to a combination of technical performance at an affordable price. As reported for other carbon-based fillers, the electrical performance depends on the aspect ratio of the conductive particles. Dawson and Adkins [65] have shown that the conduction mechanism of carbon-black filled polymers depends on the filler loading. In composites with low loadings (from 5% to 15% by volume), resistivity was due to the transfer of electrons between particles. For much higher filler loadings (50% by volume) the conductivity is related to the transport within carbon black particles. The authors achieved such results from polycarbonate-filled composites. In this context, if one considers the conduction mechanism of composite bipolar plates, it is evident that the transport of electrons within conductive fillers may be determinant for the electrical performance as the volume concentration of such particles is generally higher than 70% by volume. Debelak and Lafdi [66] obtained exfoliated graphite particles with three different surface areas. The original graphite grade was comprised of natural flake particles. They classified the exfoliated material as small ($16.02\,m^2\,g^{-1}$), medium ($15.61\,m^2\,g^{-1}$) and large ($15.35\,m^2\,g^{-1}$) particles. They prepared composites of these particles with epoxy resin and investigated the influence of the aspect ratio on the electrical behavior of the composite. The percolation threshold was found to be nearly independent of the particle surface area, being 8 wt.% for all samples. However, the aspect ratio was closely related to the electrical conductivity of the composite. It was found that the resistivity of the composite prepared with large particles, i.e., with the highest aspect ratio, was lower than that of the composites reinforced with small or medium particles.

Clingerman et al. [67] studied the electrical conductivity of carbon fiber-filled nylon 6.6 and polycarbonate composites. The mixture of the different components was performed in a conventional twin-screw extruder. After pelletizing, specimens were injection molded for the electrical measurements. The concentration of conductive fibers ranged from 10 to 50 wt.%. In the same way as Chen et al. [58], Clingerman et al. reported that high aspect ratios led to low electrical resistivity. According to Clingerman et al. [67], the difference of surface energy between polymer and filler is another critical factor for the conductivity of carbon-filled polymer composites. They stated that similar surface energies lead to better wetting of the filler by the polymer. As a result, larger quantities of polymer coat the filler surface. Consequently, the percolation threshold increases as more particles are required to form a conductive network in the structure of the composite.

Balogun and Buchanan [68] studied the percolative properties of graphite-filled CPCs. The main aspect of this article is related to the adequate dispersion of conductive particles within the polymer matrix. Randomly dispersed particles result in increased percolation volume, thus enhancing electrical performance. Logakis et al. [69] reported on the importance of keeping the aspect ratio of carbon nanotubes after processing to achieve a low percolation threshold in MWCNTs–polyethylene terephthalate composites.

Deng et al. [70] compared the percolation behavior of MWCNTs and carbon black-filled polypropylene composites. According to them, the interaction between MWCNTs in the conductive network is much stronger than between spherical particles of carbon black. This is a consequence of the higher aspect ratio and physical entanglement of the nanotubes [71]. Additionally, a high aspect ratio also
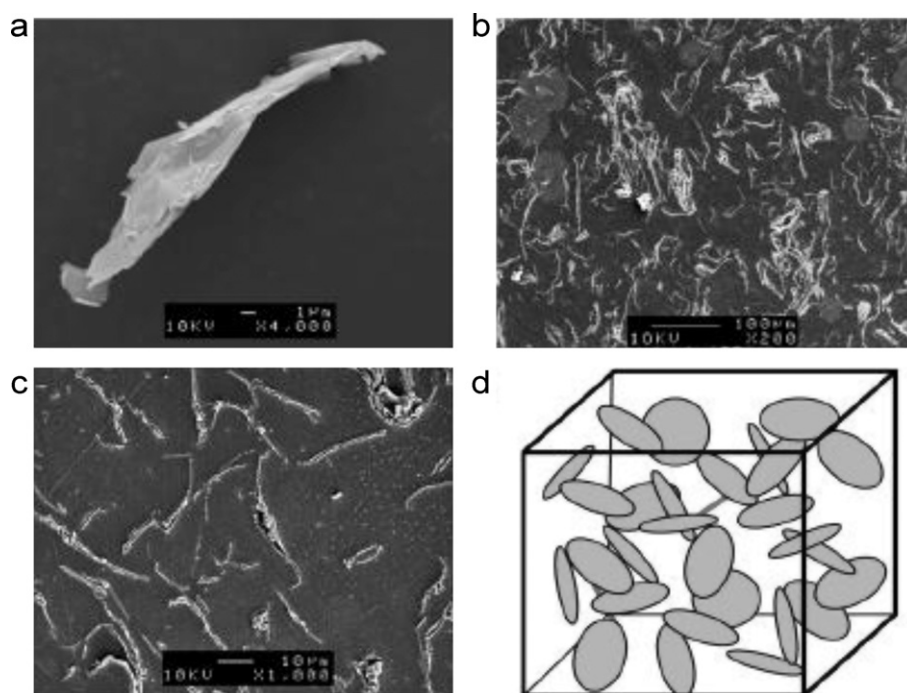
Fig. 3. SEM micrographs of (a) GNP particle; (b and c) random distribution of GNPs within epoxy matrix; (d) schematic model of GNP conductive network (Reproduced from Li and Kim by permission of Elsevier Science, UK [49].).
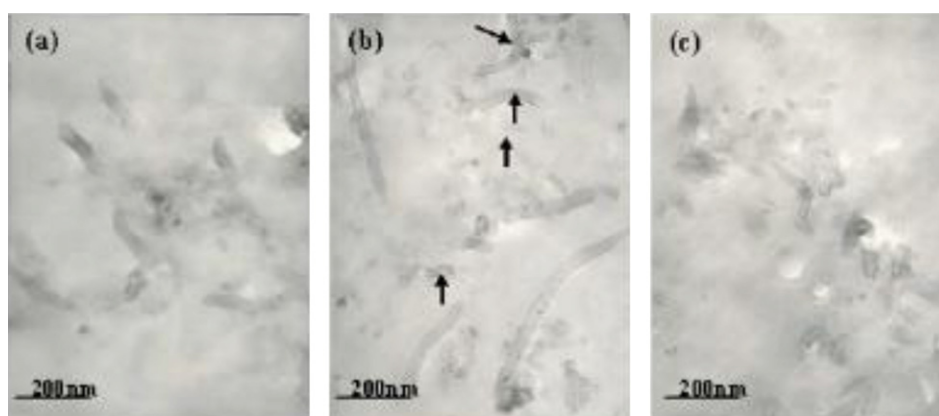

Fig. 4. TEM images of MWCNT/PVDF nanocomposites with aspect ratios of (a) 62, (b) 116 and (c) 437 (Reproduced from Yao et al. by permission of American Institute of Physics [63].).

leads to exceptionally low percolation thresholds in CNT–polymer composites [72,73]. Values as low as 0.004 vol.% have been reported [74]. On the other hand, the percolation threshold for polymer matrix composites reinforced with low aspect ratio carbon black particles reaches much higher values [75]. Deng et al. [70] gave a further insight into the understanding of the electrical performance of carbon-based polymer composites by investigating the conductivity during melt processing. It was found that carbon black particles form clusters that are more likely to break apart during melt extrusion than the entangled nanotubes.

Han et al. [76] investigated the electrical behavior of polyethylene (PE)/MWCNT and PPS/MWCNT composites prepared by melt mixing in a twin screw extruder. They identified a percolation threshold of 5 wt.% for PE based and of 3 wt.% for PPS based composites. From SEM micrographs, the authors observed that the nanotubes were more evenly dispersed in the PPS matrix than in
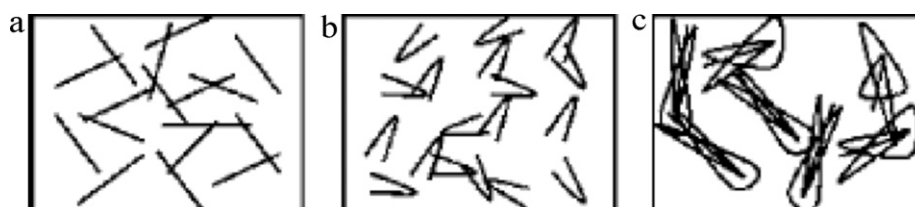
Fig. 5. Schematic representation of percolation phenomena in Fig. 4 (Reproduced from Yao et al. by permission of American Institute of Physics [63].).

the PE matrix. The lower percolation threshold of the PPS based composite was ascribed to this morphological feature.

The beneficial influence of high aspect ratio conductive particles on the decrease of the percolation threshold of CPCs was also observed for expanded graphite (EG) reinforced polymers. EG is generally formed by first submitting natural graphite to an acid treatment to produce a graphite intercalated compound. Then, this compound is rapidly heated to cause the expansion of the intercalated structure. EG maintains the layered structure of natural graphite flakes but with pores of multiple sizes and nanosheets with a very high aspect ratio. The network of pores facilitates physical and chemical adsorption between EG and the polymer while the high aspect ratio favors the electrical contact between neighboring EG particles. Zheng and Wong [77] investigated the electrical behavior of PMMA based composites reinforced with carbon black, EG and unmodified graphite particles. They observed that the high aspect ratio EG particles imparted a percolation threshold of 1 wt.%, while for carbon black and unmodified graphite the values were 8.0 wt.% and 3.5 wt.%, respectively. Zhao et al. [78] also reported a percolation threshold of only 1 wt.% for a PPS-EG composite.

The models proposed to explain the percolation behavior of CPCs are, in most cases, based on the incorporation of only one type of conductive filler within the polymer matrix. Sun et al. [79] extended the model proposed by Celzard et al. [37] to the case of polymer matrix composites prepared with two different conductive fillers simultaneously. They combined MWCNT with graphite, carbon black with graphite and MWCNT with carbon black. The model identifies the major role that the high aspect ratio MWCNT particles play on the formation of conductive networks between the fillers at low concentrations. In this way, the importance of the aspect ratio of the conductive particles is also evidenced when the polymer matrix is filled with two different types of fillers.

The total filler loadings in composite bipolar plates are much higher than the aforementioned contents that are usually needed to produce common CPCs. While for CPCs the concentration of the conductive filler is always below 10 wt.%, for composite bipolar plates this number is raised to 60–80 wt.% [80,81]. This high concentration is needed for the electrical conductivity requirements of PEM fuel cells. Furthermore, it is often reported that composite bipolar plates are comprised of more than one type of conductive filler. Natural and synthetic graphite, carbon nanotubes, carbon black, carbon fibers, expanded graphite and mixtures thereof are reported as conductive fillers for these components [82–84]. The interaction between them is determinant for the bulk electrical behavior of the composite. In this way, the electrical behavior of a low loading CPC filled with a single type of filler and that of a high loading bipolar plate filled with a mixture of different conductive particles is different, yet dependent on the same morphological feature, i.e., an effective contact between conducting particles. However, despite any discrepancy, it is possible to extract useful indications from the experimental investigations on the percolation phenomena of low loadings CPCs and use them to successfully design highly loaded polymer based composites for PEM fuel cell bipolar plates. The major finding is that high aspect ratio particles form conductive networks more effectively than spherical ones. In this way, it is highly desirable to use elongated fillers instead of round-shaped particles. Representative data from the references reviewed in this section are summarized in Table 2. The benefit of using high aspect ratio fillers such as MWCNT is evident, as the percolation threshold may be achieved at low loadings. In addition, the electrical performance of composite bipolar plates is also dependent on the intrinsic conductivity of the fillers and their sizes, as well as the nature of the polymer matrix. Moreover, it is important to consider the processing methods and conditions during the manufacturing of the composite. The next section deals with this problem, aiming to identify the main aspects of the

Table 2
Percolation thresholds of conductive polymer composites.

Reference	Matrix	Filler	Percolation threshold
[28]	Epoxy	CB MWCNT	5.00[a]2.00[a]
[36]	Epoxy	MWCNT	0.50–1.00[b]
[39]	Epoxy	MWCNT	0.0025[b]
[46]	PP	MWCNT	2.00[b]
[58]	PMMA/PVC	EG	3.50[b]
[59]	PET	Graphene	0.47[a]
[60]	Phenolic resin	EG	3.00[b]
[61]	PE	Synthetic graphite CF	50.0[b]7.50[b]
[62]	PP PP	SWCNT Flake-like graphite	4.50[a]9.30[a]
[63]	PVDF	MWCNT	0.0077[a]
[66]	Epoxy	Exfoliated graphite	8.00[b]
[68]	ABS	Synthetic graphite	0.23[a]
[69]	PET	MWCNT	0.05–0.10[b]
[71]	Epoxy	MWCNT	<0.10[b]
[73]	PP	MWCNT	0.11[b]
[74]	UHMWPE[c]	MWCNT	0.004–0.007[a]
[75]	Epoxy	Carbon black	4.00[b]
[76]	PE PPS	MWCNT MWCNT	5[b]3[b]
[77]	PMMA	EG CB Flake-like graphite	1.00[b]8.00[b]3.50[b]
[78]	PPS	EG	1.00[b]

[a] vol.%.
[b] wt.%.
[c] Ultra high molecular weight polyethylene.

structure–property–processing relationship of composite bipolar plates from particular studies focusing on the electrical performance of these components. It is intended that the information becomes a valuable tool for improving the materials selection process undertaken prior to the manufacturing of bipolar plates.

3. Electrical conductivity of composite bipolar plates

One of the main challenges of PEM fuel cell manufacturers is to maximize the power density of these devices. The pathway to reach this goal is closely related to the reduction of ohmic losses within the fuel cell stack. In this context, the optimization of the electrical conductivity of polymer matrix composite bipolar plates plays a leading role thereby demanding many efforts to the development of increasingly conductive materials. The science behind this quest is comprised of a conjunction of characteristics owing to materials, processing and their mutual interaction. The management of this complex and exciting materials science challenge is the aim of this section. Table 3 summarizes the main results from the references reviewed throughout this section. It evidences the routes for greatly surpassing the electrical conductivity target established by DOE (Table 1), depending on the filler, matrix and processing methods used in the manufacturing of composite bipolar plates.

3.1. Graphite

Polymer based composite bipolar plates achieve their electrical performance by the incorporation of specific loadings of conductive inorganic fillers. Graphite particles are the standard option to fulfill the technical requirements of conductivity at a reasonable cost. Optimization of this property is only possible if the percolation threshold of the conductive filler in the polymer matrix is known. However, the percolation threshold is only the tip of the iceberg and there is much more to consider. The intrinsic conductivity of

Table 3
Electrical conductivity (σ) of polymer–graphite composite bipolar plates.

Matrix	Filler	Filler loading	Composite preparation method	Bipolar plate processing method	σ (S cm^{-1})	Reference
PP	Synthetic graphite CB	55[a] 25[a]	Melt compounding	Compression molding	36.4[b]	[22]
PPS	Graphite	80[a]	Ball milling	Compression molding	118.9[b]	[23]
PVDF	Graphite CF	70[a] 6[a]	Wet-lay lamination	Compression molding	292[b]32[d]	[24]
PPS	Graphite CF	70[a] 6[a]	Wet-lay lamination	Compression molding	325[b]30[d]	
Phenolic resin (novolac type)	Graphite CB CF	Not mentioned 25[c] 5[c]	Preforming (mixing; pre-curing)	Compression molding	263[b]	[25]
Phenolic resin (novolac type)	Flake-like graphite EG	67.5[a] 7.50[a]	Preforming (mixing; pre-curing)	Compression molding	250[b]	[27]
Epoxy	Graphite CB	70[c] 5[c]	Mixing	Compression molding	153.8[b]	[28]
Epoxy	Graphite MWCNT	73[c] 2[c]	Mixing	Compression molding	254.7[b]	
Epoxy	Graphite CF	68[c] 7[c]	Mixing	Compression molding	237[b]	
PP	Graphite MWCNT	79.4[a] 0.80[a]	Melt compounding	Compression molding	548[b]	[29]
Phenolic resin (resole type)	Natural graphite Synthetic graphite	55[c] 10[c]	Mixing	Compression molding	45.5[b]	[30]
Phenolic resin (resole type)	Natural graphite CB	50[c] 20[c]	Mixing	Compression molding	400[b]	
Epoxy	EG	69[a]	Continuous expanded graphite sheet impregnated with resin and then cured	Compression molding	121[b]	[32]
Phenolic resin (resole type)	Natural graphite Synthetic graphite	40[c] 40[c]	Mixing	Compression molding	120[b]	[87]
Phenolic resin (novolac type)	Graphite	85[a]	Mixing	Compression molding	250[b]	[90]
PVDF	Ti$_3$SiC$_2$	70[c]	Mixing	Compression molding	350[b]	[92]
Phenolic resin (resole type)	Natural graphite CB CF	65[c] 7.5[c] 2.5[c]	Mixing resin, graphite and CB, then the slurry was applied on porous CF preform	Compression molding	303[b]	[93]
Phenolic resin (novolac type)	Flake-like graphite EG	60[a] 15[a]	Preforming (mixing; pre-curing)	Compression molding	390[b]	[95]
Epoxy	EG CB	60[a] 5[a]	Solution intercalation	Compression molding	500[b]	[97]
Phenolic resin (novolac type)	EG	50[a]	Mixing	Compression molding	280[b]	[98]
Phenolic resin (novolac type)	EG CB	50[a] 5.0[a]	Mixing	Compression molding	285[b]	[100]
Phenolic resin (novolac type)	Natural graphite MWCNT	65[c] 1.0[c]	Mixing	Compression molding	178[b]30.0[d]	[106]
Vinyl ester	Natural graphite MWCNT	70[a] 1.0[a]	Bulk molding compound	Compression molding	643[b]	[107]
Vinyl ester	Natural graphite MWCNT	70[a] 0.30[a]	Bulk molding compound	Compression molding	744[b]	[108]
Phenolic resin (novolac type)	Natural graphite MWCNT	17.1[a] 3.0[a]	Milling	Compression molding	145.2[b]	[110]
Phenolic resin (novolac type)	Natural graphite Montmorillonite	74.3[a] 1.0[a]	Bulk molding compound	Compression molding	260[b]	[115]
PPS	Mesocarbon microbeads	80[a]	Mixing	Compression molding	133.7[b]21.37[d]	[116]
Phenolic resin (novolac type)	Natural graphite	85[a]	Milling	Compression molding	142[b]	[128]

Table 3 (*Continued*)

Matrix	Filler	Filler loading	Composite preparation method	Bipolar plate processing method	σ (S cm^{-1})	Reference
Compressed expanded graphite (CEG)	Epoxy	40[c] (in the impregnation solution)	Resin impregnation + compression	Compression molding	175[b]	[130]

[a] wt.%.
[b] In-plane.
[c] vol.%.
[d] Through plane.

graphite particles depends on their nature, degree of crystallinity, size and morphology.

Wissler [85] classified graphite into natural or synthetic grades. The degree of crystallinity of natural graphite is often higher than that of synthetic products, leading to higher electrical conductivity. However, this property is dependent on the origin of natural graphite, i.e., it may be different from one extraction mine to another. Thus, flake-like natural particles extracted in China may present lower conductivity than particles of similar morphology extracted in Brazil or Canada. Furthermore, after mining, graphite crystals undergo a series of processing operations comprised mainly of milling and sieving. Then, particle morphology and size are altered during such operations and so is the intrinsic electrical conductivity. Synthetic grades may be obtained with several purities and degrees of crystallinity depending on the conditions of temperature during heat treatment and the raw materials used. This poses a wide variety of commercial products. Graphite manufacturers offer materials of various grain sizes, surface areas and intrinsic conductivities. In fact, there are many options that present higher conductivities than natural grades [86]. In this way, bipolar plate designer must be aware of these possibilities and make a judicious selection of the graphite grade regarding its nature, particle size and morphology. The accomplishment of this goal is facilitated by carefully analyzing literature data.

Dhakate et al. [87] prepared phenolic resin–graphite composite bipolar plates by compression molding. They used a mixture of natural and synthetic graphite with a total filler loading between 60 and 80 vol.%. The best electrical conductivity was achieved at 80 vol.%. In addition to the obvious effect of reducing the resin content to increase the conductivity, the authors reported on the deleterious effect of incorporating synthetic particles of lower intrinsic electrical conductivity. Moreover, the particle size of the synthetic grade was also lower than that of the natural product. As a result, synthetic particles made the interaction with phenolic resin easier when placed between the larger natural particles. Thus, they widened the more conductive natural particles, rendering the transport of electrons more difficult.

The influence of graphite particle size and morphology on the electrical conductivity of polypropylene based bipolar plates was assessed by Derieth et al. [88]. They evaluated spherical and flake-like particles at a fixed concentration of 78 wt.%. For the flake-like compound three different particle sizes were tested: 5, 10 and 20 µm. For the spherical compound only 20 µm-sized particles were assessed. It was found that the electrical conductivity of flake-like particle-filled polypropylene increased as the particle size was reduced. In the same way, flake-like particles yielded more conductive composites than spherical shaped ones. According to the authors, this result was a direct consequence of the high aspect ratio of the elongated flake-like graphite in comparison with the shorter spherical particles, thus enhancing the electrical contact between neighboring particles, as stated by the classical percolation theory [33]. Despite the beneficial effect of small conductive particles on the electrical performance of the composite, it is also important to analyze how its manufacturing characteristics are affected by graphite particle size. In this context, the authors verified that

larger particles produced a higher output rate during the extrusion process undertaken to prepare pellets for injection or compression molding. Furthermore, as the particle size increases and their surface area decreases, the amount of binder needed to produce composites with feasible rheological properties is lower than for small particles. Consequently, when larger particles are used, it is possible to raise their concentration in the composite without sacrificing moldability. This, in turn, would allow for the increase of electrical conductivity while assuring ease of manufacturing. The same considerations are valid for spherical particles in comparison with elongated flake-like products. Based on the results of Derieth et al. [88], it is clear that the processing conditions of composite bipolar plates should not be disconnected from their electrical performance. In this way, spherical particles that would not be suitable at a first glance may be attractive if the materials selection process is undertaken in conjunction with the processing methods.

Kuan et al. [89] investigated the influence of graphite particle size on the electrical conductivity of vinyl ester based composite bipolar plates. They assessed particles with sizes lower than 53 µm up to 1000 µm. It was found that the resistivity of the composite increased as the diameter of the graphite particles diminished. This tendency confirms the report from Derieth et al. [88]. According to Kuan et al. [89], the conduction of electrons is enhanced after compaction of the graphite powder due to the aggregation of the conductive particles, thus lowering the electrical resistance of the composite.

Heo et al. [90] carried out a study on the influence of graphite particle size and morphology on the electrical conductivity of phenol resin based composite bipolar plates. Spherical and flake-like particles were evaluated at a filler loading of 85 wt.%. For sphere type graphite the particle's sizes were 7, 15 and 25 µm. Flake-like particles were only 25 µm. The electrical conductivity was found to be barely dependent on the particle size of the spherical graphite particles. The most decisive factor of influence was the density of the composite that is closely related to the compactness during compression molding. Similar densities were achieved with different particle sizes leading to a homogeneous conductivity behavior. The authors explained their results by considering that the conduction mechanisms of CPCs may be described through an inter-particle or intra-particle model. Inter-particle conductivity arises from direct contact between graphite particles. It is dominant at low filler loadings. In this case, as the particle size decreases, the conductivity increases due to the effective formation of conductive networks. Intra-particle conductivity is proportional to the conductive path length within an individual particle, i.e., to the particle size. This mechanism is important at high filler loadings. A schematic representation of these mechanisms is shown in Fig. 6.

In addition to particle size, Heo et al. [90] described the major role that particle shape exerts on the electrical behavior of polymer–graphite composite bipolar plates. They showed that, at the same filler loading and particle size, sphere-type particles form point-to-point contacts with each other rather than surface-to-surface contact. As a result, the insulating polymeric phase is placed into the gaps between the graphite particles. Additionally, pores are also formed. Such non-conductive islands block the con-
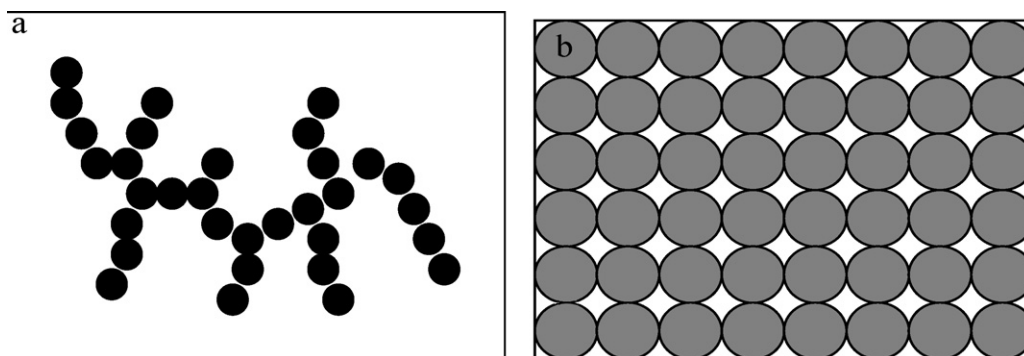
Fig. 6. Schematic representation of the conduction mechanism proposed by Heo et al. [90]: (a) low filler loading and (b) high filler loading.

nection between conductive particles, increasing the resistivity of the composite. Flake-like particles form surface-to-surface contacts instead. Hence, the formation of non-conductive regions is impeded, enhancing the conductivity of the composite.

Hui et al. [91] studied the influence of graphite particle size on the electrical conductivity of composite bipolar plates. They prepared bulk molding compounds by mixing novolac epoxy resin and natural graphite particles. According to their results, the electrical conductivity increases with the graphite particle size. This would be due to a smaller number of conductive particles as their size increases, thus lowering the contact resistance between them and, ultimately, leading to higher electrical conductivity. Chunhui et al. [80,92] have reported similar results for sodium silicate/graphite and aluminate cement/graphite conductive composites. They showed that for high filler loadings the contact resistance between conductive particles determines the bulk electrical behavior of the composite. As the surface area is smaller for large particles, they are likely to yield high conductivity composites. Other authors have also observed this behavior [93].

The results from the references described above only refer to one type of conductive filler of homogeneous size. A different approach was investigated by Chunhui et al. [92]. They evaluated the effect of the incorporation of conductive fillers with different sizes on the electrical behavior of composite bipolar plates. They proposed that the conductivity of the composite is influenced by the accumulation of conductive particles. Thus, the right size of conductive fillers would enhance the compactness of the composite, reduc-

ing its resistivity. This effect is schematically represented in Fig. 7, where D and d are the diameters of the large and small particles, respectively. The most suitable relation between the diameters of the particles was determined to be $d = 0.154D$. Then, they used two different graphite particle sizes: >90 μm and <45 μm. The electrical conductivity was found to increase when 10 wt.% of the small size particles were added to the formulation, keeping the total filler loading at 75 wt.%. For higher concentrations of the small particles the conductivity was lower than that of the composites prepared with only one particle size. According to the authors, the pore volume is reduced when one kind of the same graphite size is used. Thus, the contact area between adjacent conductive particles increases by adding the proper content of small particles into the mixture. Consequently, the conductive paths increase and the composite becomes less resistive. If, instead, the concentration of the small particles continues to augment, the primary structure of the large sized particles may be destroyed. So, the pore volume would increase, diminishing the conductive paths between graphite particles and decreasing the conductivity. This gradation of conductive fillers is barely reported in the literature. As shown by Chunhui et al. [92], it is an efficient method to enhance the electrical behavior of composite bipolar plates, since the proper size and content of small particles are identified. This is an open field of research in the PEM fuel cell area that should be extensively explored by the scientific community.

Mathur et al. [30] confirmed the validity of this approach by evaluating a mixture of natural and synthetic graphite particles in a
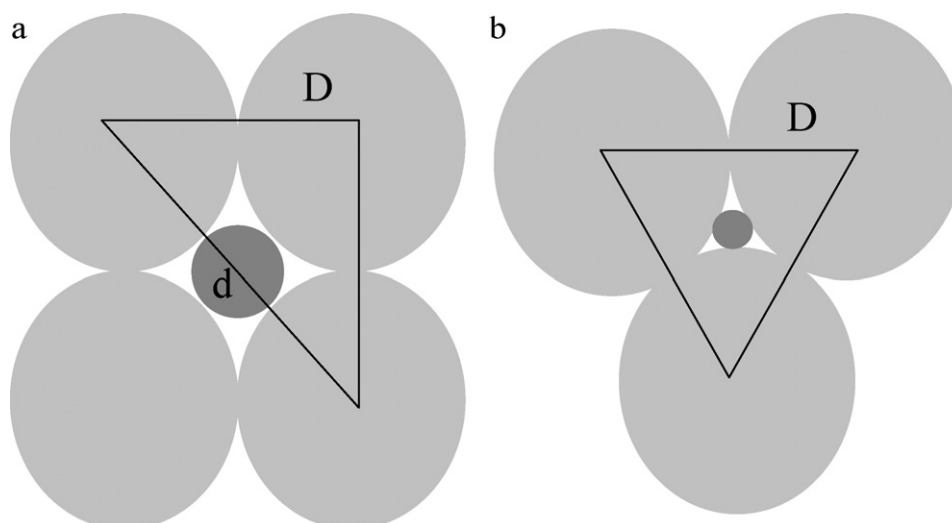
Fig. 7. Sketch of particle size gradation of two different particles: (a) loose compaction and (b) highest compaction.

phenolic resin based compression molded composite bipolar plate. The major conductive filler was natural flake-like graphite with a particle size of 75–150 μm. Synthetic particles were much smaller (<1 μm) and of higher electrical resistivity than the natural particles. The concentration of polymer was fixed at 35 vol.% and the fraction of synthetic particles varied up to 25 vol.%. Even though the intrinsic resistivity of the synthetic particles was higher than that of the natural material, the results showed that the electrical conductivity of the composite increased as the concentration of the smaller synthetic particles increased up to 15 vol.%, reaching a stable value. This effect was ascribed to the fact that the small synthetic particles filled the voids between natural graphite flakes, helping to reduce the bulk resistivity of the composite.

In addition to conventional graphite, expanded graphite emerged as a promising filler for composite bipolar plates [94,95] regarding the challenges of weight reduction and maximization of electrical performance. This material is obtained from chemical and thermal treatment of natural flakes [96]. Du and Jana [97] developed epoxy/EG composite bipolar plates that reached in-plane electrical conductivity of 1000 S cm⁻¹, far higher than the DOE target of 100 S cm⁻¹ (Table 1). However, the porous nature of the EG structure has a deleterious effect on the flexural strength of the composite. Therefore, its concentration should be controlled by considering a proper balance between electrical performance and mechanical behavior. Very scarce information on the influence of EG particle size on the electrical conductivity of composite bipolar plates is available in the literature. An exception can be found in Dhakate et al. [98]. They conducted an investigation on the influence of EG particle size on the electrical conductivity of phenolic resin based composite bipolar plates. EG particles were obtained from natural graphite of sizes 30, 50, 150 and 300 μm. The electrical conductivity of the composites was found to reach a maximum value for the specimens prepared with the higher EG particle size. This result was due to the fact that smaller particles are more numerous than larger ones. Hence, the number of contact dots between them is also higher, increasing the contact resistance and reducing the conductivity of the composite. This behavior resembles that of conventional graphite particles [92,93]. It is noteworthy that the long aspect ratio typical of EG particles favors the electrical contact between them, increasing the conductivity of the composite. The authors conducted further experiments on the electrical behavior of composites prepared with a mixture of large and small sized EG particles. They added 50 μm-diameter particles to 300 μm-based composites at concentrations ranging from 10 wt.% to 50 wt.%. The electrical conductivity was found to increase for the 10 wt.% mixed EG particle composite in comparison with the plate prepared with only 300 μm-diameter particles. Such improvement was due to the increase of the contact area between small and large EG particles as the small sized material fills the voids between the larger ones. As the concentration of the smaller particles increases, the conductivity of the composite gradually deteriorates. Above 20 wt.% of 50 μm-diameter particles the composite becomes more resistive than that prepared only with 300 μm-diameter particles. The rupture of the conductive networks between the larger EG particles by the high loadings of small sized particles would be responsible for such behavior. Thus, the explanation for the synergistic effect of the gradative fillers on the electrical properties of the EG based composite is equivalent to the model proposed by Chunhui et al. [92] to describe the same effect on conventional natural flake-like graphite based composites. The gradation of particle sizes of EG based composite bipolar plates is hardly investigated.

Selecting proper graphite grades for composite bipolar plates is crucial for the electrical performance of PEM fuel cells. A successful design may be achieved through simple considerations: to maximize intrinsic electrical conductivity of the graphite particle; for the same filler loading, the higher the aspect ratio, the higher the electrical conductivity of the composite; and to maximize particle size if only one type of conductive filler is used. However, these basic directions do not stand alone. It is of prime importance to test the synergistic effect of different particle sizes independently of the graphite nature, i.e., for natural, synthetic and expanded grades or even mixtures of them. This approach is very promising, though not deeply explored in the literature. Additionally, the designer must cope with the compromise between electrical conductivity and mechanical resistance. Actions implemented to improve the electrical behavior of graphite-based composite bipolar plates by varying structure-related parameters such as the type of filler, its concentration, morphology and size have a direct impact on the flexural strength of the composite. There is, yet, a deep dependence of the electrical properties of composite bipolar plates on the processing methods and parameters used to manufacture them. This topic is discussed in Section 3.6.

3.2. Carbon black

Carbon black has been tested as minor conductive filler in graphite–polymer composite bipolar plates. Its reduced particle size allows for the filling of voids between graphite particles, thus increasing the number of conductive paths and the bulk electrical conductivity of the composite [30,93]. Mighri et al. [99] used four different carbon blacks with distinct surface areas as reinforcements for polypropylene–graphite composite bipolar plates. They observed that the electrical resistivity decreased as the surface area of the carbon black increased. The maximum content of carbon black was determined as 18 vol.%. Higher loadings make the wetting of carbon black particles by the resin more difficult, leading to further complications during compounding such as die blockage. The beneficial effect of incorporating carbon black into graphite–polymer composite bipolar plate was also reported by Lee et al. [28]. They observed that the total filler loading required to reach high conductivity was significantly reduced when carbon black was added to the composite formulation. The small carbon black particles helped to make conducting tunnels between graphite particles, increasing conductivity. However, this behavior was found to be dependent on the concentration of CB particles. Above a critical content of 7.5 vol.% the conductivity was found to decrease as the wetting of CB particles by the resin becomes poor, impairing the compaction of the composite plate. In the same way, Dhakate et al. [87] obtained similar results for phenolic resin–graphite composite bipolar plates reinforced with carbon CB particles. In this case, the critical concentration of carbon black was 20 vol.%.

It is interesting to note the significant difference of the critical concentration values of CB particles reported in the literature. For instance, according to Lee et al. [28], this concentration was 5 vol.% while for Dhakate et al. [87] this value was 20 vol.%. Such discrepancies arise from intrinsic electrical properties and, most importantly, from morphology-related issues of both graphite and carbon black particles.

The above mentioned reports are all related to conventional natural or synthetic graphite based composite bipolar plates. Dhakate et al. [100] extended these studies to investigate the effect of incorporating carbon blacks into expanded graphite–polymer composites. They showed that the electrical conductivity of EG–polymer composite increased 15% by adding 5 wt.% of CB at a phenolic resin concentration of 45 wt.%. Upon further increase of the CB content, the conductivity diminished. The increase of conductivity was due to the formation of additional conductive paths between the small CB particles and the larger EG particles. The explanation for the increase of the resistivity above a critical concentration of CB particles was based on their agglomeration, forming multiple networks. As the intrinsic conductivity of the CB

particles was lower than that of the EG particles, the bulk conductivity of the composites decreased accordingly.

It is clear that the conductivity of composite bipolar plates may benefit from the addition of small CB particles. This effect was reported by several authors and is similar to the gradation of graphite particle sizes discussed in the previous section.

3.3. Carbon fibers

Carbon fibers are the primary source of mechanical strengthening for polymer–graphite composites. Properties such as hardness, fracture toughness and flexural strength benefit from the incorporation of these fillers. However, it should be emphasized that as the concentration of carbon fibers increases so does the hydrogen permeability of the composite bipolar plate [101]. Hydrogen permeation is related to the safety operation of PEM fuel cells [102]. Therefore, it is important to establish a compromise between mechanical performance and acceptable hydrogen permeation. Likewise, the addition of carbon fibers has a strong influence on the electrical behavior of composite bipolar plates. Mathur et al. [30] verified that the electrical resistivity of phenolic resin–graphite composites increased with the addition of carbon fibers. Individual carbon fibers presented higher resistivity than the natural graphite particles used in the manufacturing of the composite. The fibers assumed random orientation after molding. Resistivity values of each individual carbon fiber are highly anisotropic. Thus, the fibers oriented perpendicular to the direction of the electric current offer higher resistance to the transport of electrons than do the fibers that lay parallel to it. The resistivity of the composite increases accordingly. Other authors [93,99] also proved that carbon fibers diminish the resistivity of polymer–graphite composites. However, the increase of electrical conductivity of polymer–graphite composites with the addition of carbon fibers was found to be dependent on the fiber concentration, i.e., there is a percolation behavior [28].

By exploring the anisotropic character of carbon fiber-reinforced polymer–graphite composites it is possible to tailor their electrical properties. This is accomplished through the careful control of processing conditions in order to produce layers of carbon fibers that are preferentially oriented parallel to the current flow. In this way, the use of long filaments is preferred to short fibers that are randomly oriented. Kim et al. [83] and Hwang et al. [103] produced highly conductive bipolar plates through this approach. The first step was to prepare epoxy-carbon fiber prepregs with continuous fibers. This procedure yields plate-like composites comprised of highly oriented reinforcements. Then, a bipolar plate is prepared by compression molding of prepregs with graphite–polymer composite [83], layer by layer up to the desired thickness or by molding only prepreg layers [103], forming a cross-ply composite bipolar plate. The structure resulting from such processing is shown in Fig. 8. It is clear that the fibers are tightly compacted and present a preferential orientation. The results point to electrical conductivities that greatly surpass the DOE target of 100 S cm^{-1}. However, as the number of prepreg layers increase, so does the contact resistance between them. Thus, the conductivity will decrease continuously above critical filler content.

It should be emphasized that in addition to the increase of electrical conductivity, the incorporation of carbon fibers into composite bipolar plates produces outstanding flexural strength. Hwang et al. [103] reported a flexural strength of 316 MPa for their prepreg based material. This performance may not be achieved for free-carbon fibers composites. Designers must be aware of this possibility, though without neglecting the concomitant increase of hydrogen permeability that carbon fibers impart to composite bipolar plates.
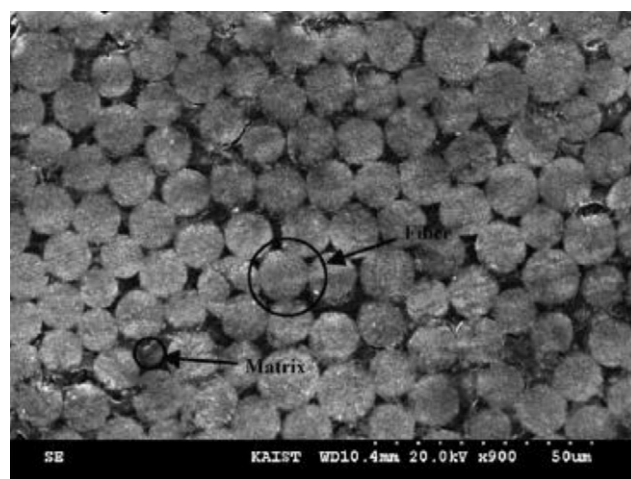
Fig. 8. SEM micrograph showing the structure of the epoxy-carbon fiber prepreg produced by Hwang et al. [103] (Reproduced from Hwang et al. by permission of Elsevier [103].).

3.4. Carbon nanotubes

The benign effect of long aspect ratio conductive fillers such as carbon nanotubes on the electrical conductivity of polymer based composites was highlighted by many authors [104,105]. As discussed in Section 2 the dispersion of CNTs in the polymer matrix is a challenging operation since they tend to agglomerate due to their high surface energy, thus impeding the formation of conductive paths that allow for the build up of enhanced conductivity. Therefore, composite bipolar plates may benefit from the incorporation of CNTs provided that they are homogeneously dispersed within the polymer matrix. Recently, Dhakate et al. [106] prepared MWCNT reinforced phenolic resin–graphite composite bipolar plates. First, they dispersed MWCNTs in toluene by ultrasonication. Then, natural graphite with a particle size of 50 μm was added to the solution and the ultrasonication was continued. The mixture was dried and ball milled with powder phenolic resin. Bipolar plates were compression molded from this mixture. Resin content was fixed at 35 vol.%. In-plane electrical conductivity was found to increase from 80 S cm^{-1} to 178 S cm^{-1} by adding 1.0 vol.% of MWCNT to the phenolic resin–graphite composite. On further increasing MWCNT content the conductivity diminished, likely due to the clustering of the nanotubes.

Liao et al. [107] focused on the use of functionalization of MWCNTs as the route to prepare highly conductive graphite–vinyl ester composite bipolar plates. Functionalization was achieved through a covalent grafting procedure of poly(axyalkylene amine) (POA) bearing maleic anhydride (MA) (named POAMA in the reference) onto HNO$_3$ oxidized MWCNTs (MWCNT–COOH groups). The treatment improves the interfacial interaction between MWCNTs and vinyl ester. The graphite powder had a particle size less than 1000 μm. First, the nanocomposites were prepared by sonication of the functionalized MWCNTs with vinyl ester resin. Then, the solution was dried and the resulting mixture was cured. The next step was to add specific quantities of graphite powder to MWCNT–vinyl ester composite and conduct a further mixing operation in a kneader, producing a bulk molding compound (BMC). The resin content in the BMC was 30 wt.%. The authors compared the electrical conductivity of composites prepared with pristine MWCNTs, oxidized MWCNTs (MWCNTs–COOH) and oxidized/grafted MWCNTs (MWCNTs–POAMA). In-plane conductivities were determined to be 643, 529 and 513 S cm^{-1}, respectively, for a concentration of MWCNTs of 1 wt.%. They observed that MWCNTs-POAMA were more evenly dispersed within the vinyl ester matrix, favoring the
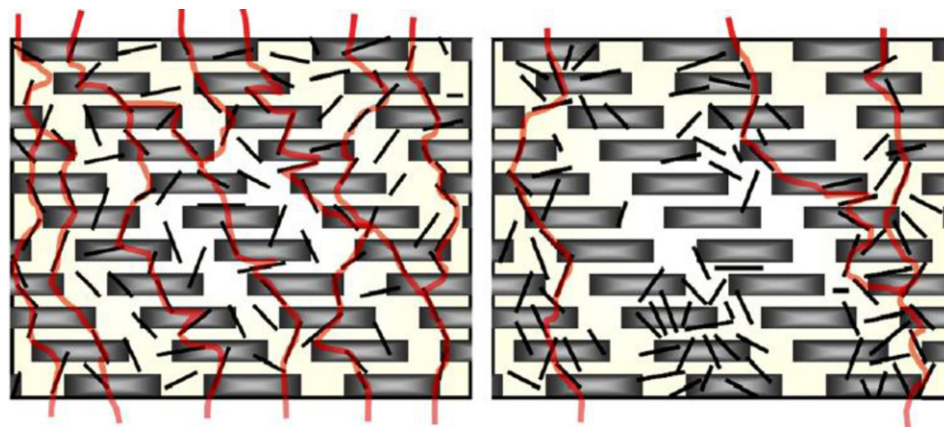
Fig. 9. Conductive mechanism in composite bipolar plates with: (a) functionalized MWCNTs homogeneously distributed and (b) clustered pristine MWCNT. Graphite (gray) and MWCNTs (black rods) forming conductive paths (curves). (Reproduced from Liao et al. by permission of Elsevier [108].).

formation of conducting networks that reduces the resistivity of the composite. It is noteworthy that the conductivities reported by Liao et al. [107] are much higher than the values achieved by Dhakate et al. [106]. The difference may be discussed based on the effectiveness of the functionalization treatment in promoting strong interaction between nanotubes and the polymer matrix allowing for their homogeneous dispersion. However, it is also important to consider the significant difference between the particle sizes of the graphite powders used by the authors. While for Liao et al. [107] graphite particle size was less than 1000 μm, for Dhakate et al. [106] it was only 50 μm. As discussed in Section 3.1, graphite particle size strongly affects the electrical conductivity of polymer based composites. Indeed, it is well documented that large particles favor the conductivity of the composite due to the decrease of the contact resistance between adjacent conductive filler at the high loadings typical of bipolar plates. Moreover, it is also reported that the incorporation of small-sized conductive fillers may give further improvement to the conductivity of graphite–polymer composites by the formation of additional electrical contacts that facilitate the transport of electrons. The formation of these additional percolating sites would be more prominent on the composites prepared by Liao et al. [107] than on those prepared by Dhakate et al. [106] due to the effective dispersion of the functionalized MWCNTs within the polymer matrix.

In a previous work, Liao et al. [108] showed the effectiveness of using poly(oxypropylene) diamines to functionalize MWCNTs, enhancing their interaction with vinyl ester resin and facilitating their dispersion within vinyl ester–graphite composites. They proposed a mechanism to explain the electrical conductivity of the MWCNT reinforced composite that is schematically shown in Fig. 9. Non-conductive polymer-rich regions are filled with graphite particles and nanotubes. MWCNTs are at the boundaries of the graphite particles. Functionalized MWCNTs that are homogeneously distributed within the polymer matrix form continuous paths to the flow of electrons. Conversely, pristine MWCNTs form clusters that yield few conductive paths.

Functionalization enhances the interaction of MWCNTs within polymer matrices. Similarly, the degree of crystallinity of the resin was found to be closely related to the dispersion of nanotubes [29]. Highly crystalline polymers present strong van der Waals forces between intermolecular chains. MWCNTs tend to aggregate within such matrices. For low crystallinity polymers the dispersion of MWCNTs is favored. These findings have been confirmed by other authors [23,109].

Despite the fact that functionalization diminishes the tendency of clustering of CNTs, some treatments may deteriorate the nanotubes' walls, thus reducing their ability to impart high electrical

conductivity [110]. Outstanding values of electrical conductivity may be achieved through the careful modification of CNTs by suitable surface treatments. However, it is important to realize that the processing of bipolar plates becomes more complex as the necessity of using functionalized CNTs arises. Consequently, this may adversely affect the overall manufacturing cost of these components. Alternatives for achieving high conductivities with pristine CNTs are to assess the influence of the degree of crystallinity of the polymeric matrix and to combine their use with graphite powders of large particle size.

3.5. Polymeric materials

From the discussion presented in the previous sections it is clear that the electrical performance of composite bipolar plates is determined by the conductive fillers added to their formulation. However, the polymer matrix used to bind the fillers also influences the electrical behavior of the composite. Furthermore, the type of polymer determines the processing method of bipolar plates and their recyclability. Both thermoplastic and thermosetting resins may be selected, depending on the criteria adopted by the designer. Thermoplastics based bipolar plates are fully recyclable. However, before being removed from the mold, they must solidify to achieve suitable mechanical strength. This is carried out from a cooling step that increases the production cycle of a single component. Thermosets, on the other hand, are not recyclable after curing in the mold. However, once cured through the action of pressure and heat, they do not need to be cooled before being removed from the mold. As a result, the production cycle is faster than that of thermoplastics, as the cooling step is eliminated. Therefore, the manufacturing cost of thermosets based composite bipolar plates is diminished. Yet, sometimes it is necessary to conduct a post-cure reaction to eliminate residual monomers that could poison the membrane electrode assembly of the PEM fuel cell, decreasing their ionic conductivity. This is especially true for phenolic resin based components [111]. Furthermore, the electrical performance of composite bipolar plates is influenced by their manufacturing processes. The next section deals with this problem. In this section, the electrical conductivity of bipolar plates prepared with several types of polymeric matrices is reviewed.

Wetting of the filler surface by the polymer depends on their surface energies. If the difference between the surface energies of polymer and filler is small, then the filler will be efficiently wetted by the resin. As a consequence, more resin will be necessary to coat the filler surface. Then, the concentration of fillers should increase before the particles come in contact with each other. Thus, the percolation threshold of the composite and its resistivity increase

accordingly. Therefore, it is important to use resins that present higher surface energy than the conductive fillers used to manufacture composite bipolar plates in order to minimize this effect [22].

Dhakate et al. [87] assessed the in-plane electrical conductivity of resole (liquid) and novolac (powder) phenolic resin based composite bipolar plates. They prepared three series of specimens: S1 was comprised of resole type phenolic resin, natural graphite and synthetic graphite particles; S2 was comprised of novolac phenolic resin, natural graphite, carbon black and carbon fibers; and S3 had the same composition of S2 but higher compaction pressure during compression molding. According to the authors, novolac resin is easy to mix with the fillers yielding a more homogeneous composite. They achieved $120 \, S \, cm^{-1}$ for the electrical conductivity of S1 composites (for 20 vol.% of resin), $160 \, S \, cm^{-1}$ for S2 and $250 \, S \, cm^{-1}$ for S3 specimens (with 35 vol.% of resin for both S2 and S3 specimens). The more uniform distribution of fillers into the novolac matrix was responsible for the higher electrical conductivity of S2 and S3 composites. The excellent behavior of S3 specimens would be due to the high compaction pressure that enhances the electrical contacts between adjacent conducting particles. Resole type resin produced the lowest conductivity specimens due to the formation of isolated polymer regions that block the transport of electrons between graphite particles.

The electrical conductivity of polypropylene/graphite composite bipolar plates was evaluated by Dweiri and Sahari [22]. Polypropylene has intrinsic low conductivity due to the absence of any polar groups in its backbone that renders the homogeneous dispersion of graphite layers more difficult [112], producing low conductivity composites. They aimed to improve the electrical behavior of the composites by the incorporation of carbon black and polyaniline (PANi). PANi is a well known conductive polymer comprised of conjugated bonds that favor electron movement [113]. The conductivity of polypropylene–graphite composites was determined to be $23 \, S \, cm^{-1}$ for solution blended plates at 80 wt.% filler loading. The addition of 5 wt.% carbon black to the polypropylene–graphite composites maintaining the resin content at 20 wt.% increased the conductivity to $36 \, S \, cm^{-1}$. The composites prepared with polypropylene, graphite and PANi presented a maximum conductivity value of $13 \, S \, cm^{-1}$. This low value was a consequence of thermal degradation of PANi during the melt compounding process used to prepare the composite plates. It is interesting to note that the conductivities of the polypropylene based composites developed by Dweiri and Sahari are significantly lower than the values of the phenolic resin based composites prepared by Dhakate et al. [87]. Even the incorporation of additional conductive filler such as carbon black was not sufficient to raise the conductivity up to the levels reported for the phenolic resin based plates of Dhakate et al. [87]. This is a manifestation of the fact that polymers with polar atoms or a single electron or pair of single electrons in their molecular configuration are easy to polarize or delocalize. Consequently, in this kind of polymer the formation of electrical channels is favored, thus enhancing the electrical conductivity of the composite. Phenolic resins have polar groups and double bonds in their molecules and are a good example of polymers in which this mechanism is active [114]. Other authors confirmed the high conductivity of phenolic resin based composite bipolar plates [25,27,93]. It is evident, by this analysis, that the nature of the polymeric resin should be a major concern for the bipolar plate designer in order to accomplish optimized electrical performance. Nevertheless, even if a resin with intrinsic low conductivity is used, such as polypropylene, it is possible to increase the electrical performance of composite bipolar plates prepared with such materials by the judicious combination of high conductivity fillers such as CNTs and polymeric matrices with a low degree of crystallinity. Liao et al. [29] have proved this assump-

tion by adding MWCNTs to polypropylene–graphite composites. They achieved electrical conductivities as high as $548 \, S \, cm^{-1}$ for the specimens prepared with low crystallinity resin and MWCNT. For the composites prepared with graphite and polypropylene (without MWCNT) the conductivity reached only $150 \, S \, cm^{-1}$ at a resin content of 20 wt.%. So, the effect of MWCNTs was preponderant to the electrical behavior of the composite. Yet, it is also clear that it is possible to achieve much better performance than reported by Dweiri and Sahari even with composite bipolar plates prepared with polymers that do not contain polar groups in its backbone such as polypropylene. In this case, the combination of high conductivity fillers, low crystallinity resins and adequate processing conditions is decisive to maximize electrical conductivity.

In addition to phenolic resins vinyl ester is often reported as a thermoset matrix for composite bipolar plates. Yen et al. [115] produced vinyl ester based composite bipolar plates with in-plane electrical conductivity of $312 \, S \, cm^{-1}$. They prepared a BMC from vinyl ester (25 wt.%) and graphite powder with a large particle size ($<1000 \, \mu m$). The same group [107,108] increased the content of vinyl ester in the BMC up to 30 wt.%, maintaining the graphite particle size. The electrical conductivity was determined to be $150 \, S \, cm^{-1}$. In this case, they incorporated functionalized carbon nanotubes into the composite formulation, reaching electrical conductivities in excess of $700 \, S \, cm^{-1}$. This outstanding performance suppresses the results obtained from phenolic resin or thermoplastic based composite bipolar plates. Similar values have been reported for epoxy resin-expanded graphite bipolar plates with the incorporation of carbon black as minor conductive fillers [97].

Some authors have tried to take advantage of the high mechanical strength and thermal stability of polyphelene sulfide (PPS) as a thermoplastic matrix for composite bipolar plates [23,116,117]. The best in-plane electrical conductivity was reported by Huang et al. [117] that used a wet-lay (paper making) process to prepare PPS containing sheets. These sheets were subsequently stacked and compression molded, forming bipolar plates with in-plane electrical conductivity of approximately $270 \, S \, cm^{-1}$. Cunningham and Baird [24] gave further improvement to the value of this property by using a lamination method, reaching $325 \, S \, cm^{-1}$.

From the results outlined above it is evident that bipolar plates based on thermosetting resins may achieve higher electrical conductivities than those based on thermoplastic matrices. However, the selection of the polymeric material should be regarded as a broader action that comprises the influence of the aspect ratio of the conductive fillers and their dispersion within the organic matrix. Independent of the type of polymer, it is found that using graphite powders of large particle size increases the electrical conductivity of the composite. In the same way, the addition of minor quantities of high aspect ratio fillers such as carbon nanotubes enhances the conductivity whether the matrix is a thermoplastic or thermoset provided the fillers are evenly distributed in it. In this context, processing methods play a major role in order to accomplish the best overall electrical performance from the individual properties of each component in the composite formulation. Some examples of how processing of composite bipolar plates determines their bulk electrical conductivity are described in the next section. Furthermore, the pathways to the successful design of composite bipolar plates from a manufacturing standpoint are discussed.

3.6. Processing methods

Manufacturing methods and processing conditions of composites affect the orientation, dispersion and interparticle distance within the polymer matrix. Additionally, molding processes may alter the aspect ratio of conductive fillers, enhance their interaction with the matrix and change the degree of crystallinity of the matrix [118–120]. These factors are closely related to the per-

colation threshold of the filler in the organic matrix and to the bulk electrical conductivity of the composite. Thus, the electrical performance of a conductive polymer composite is a function of the manufacturing method. Inadequate conditions may destroy the possible positive effects even of the most conductive filler. An overview of different processes used to fabricate composite bipolar plates, their capabilities and limitations is given in this text. This information is intended to be viewed as a tool to help the bipolar plate designer in the selection of the manufacturing process and conditions, facing specific requirements of different types of matrices and reinforcements.

Injection molding is thought of as an attractive manufacturing method for composite bipolar plates due to the high productivity inherent to the process that favors the massive production rates necessary to reduce production costs. However, high loadings of conductive fillers dispersed into the polymeric matrix increase the viscosity of the mass to be injected, thus making the process more difficult. Furthermore, the electrical conductivity of injected composites is negatively affected because of the high shearing typical of the process [121]. This shearing promotes the rupture of conductive particles, altering their aspect ratio and morphology. Therefore, the adequate initial selection of filler particle size and shape may be hampered by the injection molding process. Reports on injection molded bipolar plates [122,21] evidence the need for improving the electrical performance of the injected components. This achievement is restricted by the intrinsic limitations of injection molding. In this way, other processes have been tested for the manufacturing of composite bipolar plates, avoiding the handicaps of injection molding but faster than conventional compression molding. An example is the wet-lay (paper making) production process described by Huang et al. [117].

The importance of obtaining well-dispersed conductive fillers within the polymeric matrix was shown by Dweiri and Sahari [22]. They prepared compression molded polypropylene-graphite composite bipolar plates. Two different methods were used to prepare the composite formulation before compression molding: melt compounding and solution blending. The conductivity of the specimens was higher for those prepared from solution blended mixtures. Mixing the components in a homogeneous way was difficult during melt compounding, thus reducing the conductivity of the composite. The solution blending method led to the production of well-dispersed mixtures, favoring the formation of conductive paths. However, solution blending has the disadvantage of disposing organic solvents after the process.

Kalaitzidou et al. [123] investigated the effect of the compounding method on the electrical behavior of polypropylene-graphite composites. They developed a process to coat the polymer with graphite nanoplatelets. It consisted of the dispersion of the nanosized filler in isopropyl alcohol, followed by sonication during a specific period of time at room temperature. Then, polypropylene in powder form was added to the solution following another period of sonication. After evaporation of the solvent, the coated polymer was obtained. The sonication step was efficient at dispersing the clusters of graphite nanoplatelets. Next, the resulting material was compression molded, obtaining composite sheets. Other specimens were prepared through conventional direct melt mixing conducted in a twin screw extruder or solution mixing and then compression molding. The percolation threshold of the specimens prepared by the coating method was the lowest, as well as the electrical resistivity. Dispersion of the agglomerated particles of graphite nanoplatelets during the sonication steps of the coating method led to the formation of a uniform layer of conductive filler at the surface of the organic matrix. Moreover, the morphology of the nanosized fillers was preserved as no shearing was used during the processing, i.e., the high aspect ratio was unaffected.

Wakabayashi et al. [124] achieved well-dispersed graphite nanoplatelets–polypropylene composite through the solid-state shear pulverization (SSSP) method. They employed a modified twin-screw extruder that applies shear and compressive stresses to solid-state materials. First, polymer and graphite were simultaneously pulverized. Then, this powder was fed to the modified extruder completing the SSSP process. After processing, the aspect ratio of the nanoplatelets was high. The authors evaluated mechanical properties but not electrical conductivity. SSSP proved to be efficient in enhancing the impact and tensile strength of the composite in comparison with specimens prepared from conventional melt extrusion. The uniform dispersion of the conductive filler in the nanocomposite was responsible for such behavior. Thus, it is expected that SSSP may act in a similar way in the electrical behavior of the composite. Further investigations are needed to confirm this possibility. If graphite nanoplatelets are envisaged as reinforcements of composite bipolar plates, SSSP should be considered as a promising manufacturing method.

The strong influence that the dispersion of conductive fillers has on the electrical conductivity of conductive polymer composites is undeniable. However, despite being commonly neglected, orientation of the filler within the polymer matrix is also of great importance. Consequently, as different manufacturing methods may impart different orientations of the dispersed fillers, it is worth evaluating their effect on the bulk conductivity of the composite. In this way, Du et al. [125] investigated the effect of filler orientation on the conductivity of SWCNT/PMMA composites. First, they mixed the nano-filler with the polymer matrix through a coagulation method that yielded a uniform dispersion of the nanotubes. Next, they prepared composites through compression and injection molding. Then, they compared the electrical conductivity of the specimens obtained from the two manufacturing methods, trying to identify the influence of the orientation of the nanotubes on this property. They defined an alignment percolation behavior, similar to the concentration percolation behavior. The conductivity would be favored in composites with a more isotropic character as the filler loading increases. In this way, the conductivity of compression molded bipolar plates would be favored in comparison with highly oriented injection molded components. In another work [126] Du et al. showed that at a fixed composition the alignment of nanotubes reduces the number of tube-tube contacts. Kim and Macosko [127] confirmed that the alignment of conductive particles diminished the number of percolating paths.

Yang and Shi [116] studied the influence of molding time on the in-plane electrical conductivity of compression molded PPS-mesocarbon microbeads composite bipolar plates. Molding time refers to the period when the highest temperature and pressure are held during compression molding. Conductivity was found to increase with molding time from 10 min to 30 min. Above 30 min there was no significant effect on the conductivity of the composite. Yin et al. [128] investigated the effect of both temperature and molding time on the electrical behavior of compression molded phenol formaldehyde/graphite composite bipolar plates. As a thermosetting matrix, phenol formaldehyde gained further improvements in mechanical strength as the molding time increased because of the higher degree of crosslinking. The optimum molding temperature was determined to be 240 °C. At this point, cure of the resin is completed, forming a three-dimensional network that favors the transport of electrons between the conductive fillers. At higher temperatures degradation of the resin diminishes the conductivity of the composite. In the same way, the conductivity reaches a maximum at a specific molding time (between 45 and 60 min) above which it drops sharply due to the increase of porosity in response to the degradation of small molecules in the structure of the composite.
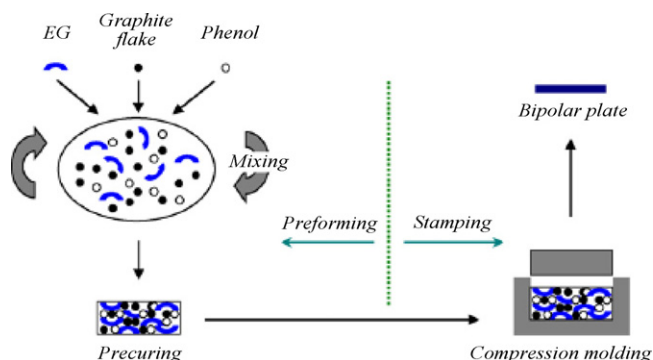
Fig. 10. Preforming manufacturing process developed by Heo et al. (Reproduced from Heo et al. by permission of Elsevier [27].).

As molding temperature and time may influence the conductivity of composite bipolar plates produced by compression molding, so does molding pressure. Bin et al. [129] assessed the effect of this parameter on the conductivity behavior of polyvinylidene fluoride/titanium silicon nitride compression molded composite bipolar plates. As expected, the conductivity increased with molding pressure due to the reduction of porosity in the composite as well as the contact resistance between conductive titanium silicon nitride particles. The authors complemented their investigation by evaluating the dependence of electrical conductivity on the molding time. The composites became more conductive with increasing molding time. The explanation for such behavior was based, as in the case of increasing molding pressure, on the reduction of porosity in the composite and of contact resistance between the conductive filler particles.

Heo et al. [27] proposed an alternative manufacturing method to produce phenolic resin–graphite composite bipolar plates. Initially, they mixed natural flake graphite, expanded graphite and phenolic resin powders. This mixture was pre-cured in an aluminum mold. These steps comprised what the authors named as the preforming process. The preformed plate was then inserted into a heated steel mold, completing the curing of the phenolic resin. This step was identified as the stamping process. The manufacturing is schematically shown in Fig. 10. According to the authors, the process is faster than conventional compression molding, allowing for the production of bipolar plates in an economical way, without sacrificing the electrical performance. The preforming step conditions, i.e., pre-curing time and pressure, presented little influence on the conductivity of the composite. During the stamping process, curing time and molding pressure presented optimum values that maximized the electrical conductivity of the composite. These values corresponded to the formation of effective conductive networks between graphite particles.

Vacuum resin impregnation were used to produce epoxy-expanded graphite composite bipolar plates [32,130]. The process aims to improve physical properties of bipolar plates by the increment of distribution of expanded graphite within the polymer matrix. Electrical conductivities above $100\,S\,cm^{-1}$ were obtained, confirming the suitability of the impregnation method for the production of composite bipolar plates.

The decision on the manufacturing process to be chosen to produce bipolar plates depends, surely, on economical criteria. However, it should not be disconnected from the materials science and engineering concepts involved in the attributes of a particular processing method. These concepts relate to filler dispersion within the matrix, preservation of filler morphology and size and degree of orientation after molding. Moreover, it is important to control process parameters such as temperature, pressure and molding

time, as they affect the crystallinity of the organic matrix, the curing of thermosetting resins and the compactness of polymer based composite bipolar plates. The final processing conditions should be carefully defined through specific experimental investigations, regarding both polymer and filler type to achieve the best electrical performance without sacrificing mechanical strength and gas permeability.

4. Recommendations for future work

Future directions in the development of polymer–graphite composite bipolar plates should encompass the compromise between materials properties and manufacturing methods. Careful analysis of the scientific literature evidences that the electrical performance of bipolar plates is strongly influenced by the dispersion of conductive particles within the polymer matrix. In this way, even the most conductive filler may not impart low resistivity to the composite if it does not form sufficient percolating sites throughout its structure. In this way, the main focus of research should be on the preparation of the composite by a judicious mixing of fillers and resin and, in a next step, on the molding of the bipolar plate. This step must receive special attention in order to not to destroy the morphology of the conductive particles. Excessive shearing during processing should be avoided. In this context, it not surprising that the most conductive composite bipolar plates reported in the literature are processed by compression molding based techniques rather than by injection molding. However, this approach establishes conflicting interests, that is, while avoiding injection molding is beneficial to the conductivity of the bipolar plate it also determines the option for a less massive production method based on compression molding. Consequently, the perfect scenario for the future would be to develop a suitable balance between performance and productivity. Regarding this trade-off, the literature presents interesting results from wet-lay (paper making) processes. Resin transfer molding may be an interesting option as it increases productivity in comparison with compression molding, without the excessive shearing of injection processes. Despite such attractive characteristic it is not explored in the literature.

In addition to the final processing of composite bipolar plates, preliminary steps comprising the mixture of materials during the preparation of the composite should be highlighted as a fundamental part of the manufacturing process. This is especially true when nanosized fillers such as carbon nanotubes are used as reinforcements. It is found that the incorporation of such fillers within polymer–graphite composites may greatly enhance the electrical performance. This accomplishment only manifests if the nanotubes are well dispersed within the polymer matrix. This is a difficult task, as they tend to agglomerate during mixing operations. The electrical performance of composite will be increasingly enhanced by developing suitable chemical agents that diminish the surface energy of carbon nanotubes, facilitating their homogeneous dispersion within the organic phase.

Mixing conductive fillers with different particle sizes may produce highly conductive composite bipolar plates. This approach is little studied for different polymer matrices. The electrical conductivity of the composite may be strongly enhanced by using suitable combinations of large and small particles. The particles may be of the same nature or not. For instance, it is a possible mix graphite of different particle sizes or graphite and carbon blacks. These options should be investigated for different graphite grades and polymer combinations. Furthermore, by combining this approach with the addition of carbon nanotubes the electrical performance of composite bipolar plates may be further improved.

5. Conclusions

Electrical conductivity of carbon–polymer composite bipolar plates can be favorably tailored through the correct choice of materials and manufacturing methods. The knowledge of materials properties is the basic tool to start a successful project. This is the driven force that guides the selection of inherent highly conductive fillers and less resistive polymeric matrices. In this way, it is necessary to understand how different carbon based fillers behave owing to the percolation phenomena in specific organic matrices. The development of composite bipolar plates may be guided by the following conclusions:

- The aspect ratio of the conductive particles should be maximized in order to reduce the percolation threshold and increase the electrical conductivity of the composite.
- Elongated particles tend to be more conductive than round fillers. In this context, graphite nanoplatelets and carbon nanotubes play leading roles on the enhancement of the electrical performance of composite bipolar plates. Similarly, flake like graphite particles are preferred to spherical ones.
- Particle size should be maximized for a given content of conductive filler.
- The effectiveness of incorporating carbon nanotubes into polymeric matrices depends on their adequate dispersion. Functionalization may be used to diminish the tendency of nanotubes to form clusters that hamper their homogeneous distribution, decreasing electrical conductivity.
- Carbon blacks are less conductive than nanotubes but may enhance the electrical properties of composite bipolar plates as minor fillers, forming additional conductive networks between graphite particles.
- The effect of carbon fibers on the electrical conductivity of composite bipolar plates is strongly related to their orientation and, thus, on the manufacturing method.
- The addition of minor quantities of small particles into mixtures comprised mainly of large conductive particles may increase the number of percolating paths, augmenting the conductivity of the composite.
- Thermosetting or thermoplastic resins containing polar groups or conjugated bonds favor the transport of electrons, thus imparting less bulk resistivity to the composite.
- It is essential to guarantee suitable dispersion of the conductive fillers within the polymer matrix by the judicious choice of the manufacturing method. Processing methods that submit the composite to excessive shearing may alter filler morphology and particle size, destroying their capability of providing high electrical conductivity.
- Poor dispersion favors the agglomeration of the conductive particles, thus reducing the formation of percolating networks and the bulk conductivity of the composite.

Acknowledgements

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